

Waterborne Polyurethanes Polyurethane Research



Bayer Polymers

WATERBORNE POLYURETHANES*

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*Excerpt from "Advances in Urethane Science and Technology", K. C. Frisch and D. Klempner, Editors, vol. 10, pp. 121-162 (1987).

I. INTRODUCTION

Waterborne polyurethanes (PUR) are not simply scientific curiosities but rather viable commercial industrial products. The earliest application areas for this class of polymeric materials were as coatings and adhesives. Here the use of solvents was precluded due to either the sensitivity of the substrate towards solvent attack or because of the flammability of the solvents. These waterborne products have now begun to penetrate application areas previously serviced only by solventborne polymeric resins.

There are three major reasons why aqueous polyurethanes forced their way into the marketplace. First of all, government agencies have placed more emphasis on the reduction of solvent emissions into the atmosphere. Secondly, the price of these solvents has escalated at a rapid pace. But perhaps most importantly, the quality of these waterborne PUR has made them very suitable for a myriad of application areas.

A wide variety of properties known from polyurethane chemistry and technology are also achievable from an aqueous medium. Waterborne PUR can be formulated into coatings and adhesives containing little or no cosolvent and which form films at ambient temperatures. They are not aggressive towards plastic surfaces and they exhibit excellent adhesion to many surfaces including glass and polymeric fibers.

Most work with aqueous polyurethanes has been done in industrial laboratories. More than 800 patents have been issued in the ca. forty years of their existence. In a recent article (1), Dieterich listed the number of pertinent patent applications per year through 1976. This chart was completed, including those listed in Chemical Abstracts as of July 1985. A major portion of the newer patent literature concentrates on tailormaking aqueous polyurethanes for specific end uses.

Table I. Patent Applications in the Area of Waterborne Polyurethane Dispersions.

| <u>Time Period</u> | <u>No. of Applications</u> | <u>Applications Per Year</u> |
|--------------------|----------------------------|------------------------------|
| 1943-1961 | 30 | 1.6 |
| 1962-1966 | 131 | 26 |
| 1967-1971 | 215 | 43 |
| 1972-1976 | 198 | 40 |
| 1977-1981 | 156 | 39 |
| 1981-1985* | 129 | 38 |

*Annualized based on July 1985 figures.

This article will focus on these newer areas. Whenever newer patents were granted in the same area as previous ones, the older reference will be omitted. Preference will be given to U.S. or German patents if equivalent patents appear also in other countries. Only the date and company to whom the patent was assigned will be referenced.

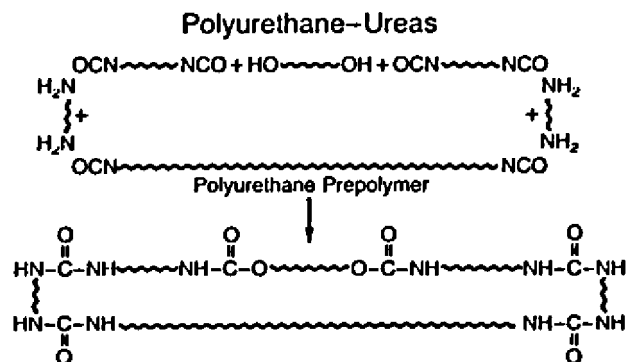
It will be necessary to set the stage by repeating some information already reported by Dieterich and Reiff in this series (2) as well as in other journals (3). The interested reader can also find an excellent summary of not only the chemistry, but also the application methods/areas for aqueous polyurethanes in a recently published book (4).

II. RAW MATERIALS

A. Basic Polyurethane Building Blocks

The chemical components from which aqueous PUR-dispersions can be obtained have been described extensively in previous publications (2,5,6). Only some basic chemistry will be reviewed here.

The typical waterborne PUR is actually a polyurethane-polyurea, i.e. a polymer which is characterized by the occurrence of both urethane (-NH-CO-O-) and urea (-NH-CO-NH-) groups in a macromolecular chain. These groups are formed by the well known polyaddition reactions between polyisocyanates and polyols leading to polyurethane segments, and between polyisocyanates and polyamines leading to polyurea segments (7, 8).



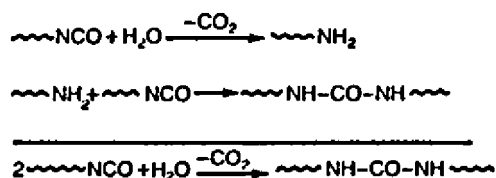
As PUR-dispersions are formed in an aqueous medium, a third reaction comes into play: the reaction of isocyanates with water. Water hydrolyzes isocyanate groups yielding amines via the unstable carbamic acid with evolution of carbon dioxide.

Water Reaction With Isocyanates



The so-formed amino groups can react with remaining isocyanate groups, yielding urea linkages and thus contributing to the extension of the macromolecular chain. A high concentration of urea groups in the polyurethane is desirable, because these groups contribute greatly to the typical properties of high performance PUR-systems.

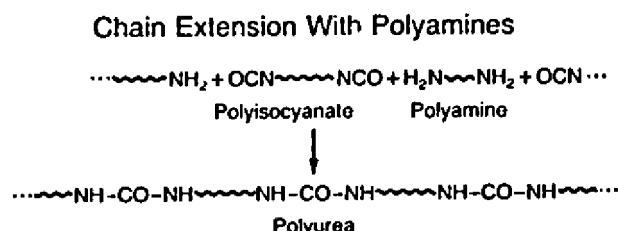
Chain Extension With Water



The selection of polyisocyanates, polyols and polyamines suitable for the production of waterborne polyurethanes is essentially the same as that known from conventional PUR-chemistry. Nearly any known type of polyisocyanates (especially cycloaliphatic diisocyanates) has been described for use in PUR-dispersions. The major feature is that the isocyanate must exhibit sufficient stability towards water during processing. Aromatic polyisocyanates, which in earlier stages of PUR-dispersion chemistry were neglected due to their high reactivity with water, can be used if suitable preparation processes are followed.

On the polyol side, the wide range of linear or slightly branched polyether, polyester and polycarbonate polyols, which are commercially available today, can be used for waterborne PUR. Short chain diols and triols are also used to adjust the urethane group content and polymer branching. In order to impart special properties, the use of several other polyol types has been described, such as epoxy-resins, hydroxy-acrylates, or oil-modified alkyd resins. Part of the polyol building blocks can be replaced with water resistant ones like hydroxylfunctional polybutadienes (9) or fluoroalkyl-containing ones (10).

The isocyanate/water reaction is minimized during the production of high performance PUR-dispersions. This is mainly because of the undesirable CO_2 evolution which results in severe foaming. Moreover, waterborne PUR which have been built up predominantly by "water chain extension" are in most cases inferior in polymer performance to those chain extended by polyamines. During water extension, two NCO-groups yield only one "valuable" urea group, whereas each NCO-group is transformed into an urea linkage upon amine extension.



In order to fully understand the modern manufacturing processes for aqueous PUR-dispersions, it is important to be aware of the reactivity differences which the described starting materials show when reacted with isocyanates. Amino groups, especially those bound to aliphatic residues, react with the NCO-function orders of magnitude faster than water does. Therefore, it is possible to perform an amine chain extension of a polyisocyanate in the presence of water.

Among the polyamines, which normally serve as chain extending agents in PUR-dispersion chemistry, the aliphatic or cycloaliphatic di- or triamines are clearly preferred over the aromatic ones. Even amino-terminated polyethers have been used (11). The primary reason is the high reactivity of the aliphatic amines with isocyanates which results in the already described advantage over the NCO-water reaction. Hydrazine or its derivatives are also valuable chain extending agents.

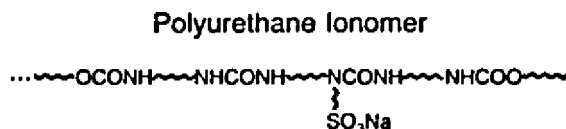
B. Internal Emulsifiers

Aqueous PUR-dispersions can basically be prepared by emulsification of hydrophobic polyurethanes in water with the aid of protective colloids or suitable external emulsifiers (12, 13). But, the unique method of dispersing polyurethanes is with built-in hydrophilic groups. The main advantages of this route are: dispersing processes which do not require strong shear forces, finer particle size, better dispersion stability, and reduced water sensitivity of the polymers obtained after evaporation of the water.

Building hydrophilic groups into the macromolecular PUR-chain means replacing a small portion of the aforementioned polyols, polyamines or polyisocyanates by special materials, which contain in their molecular structure ionic groups, ionic group precursors, or other water soluble segments. These special building blocks are called "hydrophilic monomers" or "internal emulsifiers".

B. 1. Ionic Internal Emulsifiers

The use of internal emulsifiers with ionic groups results in the formation of PUR-ionomers (14, 15). The following schematic formula shows, as an example, a section of a typical polyurethane-polyurea with lateral sulfonate groups.



In order to obtain stable aqueous dispersions, a content of usually 1% or less by weight of salt groups in the polyurethane is sufficient (16). This means that the hydrophilic ionic groups are distributed within the large hydrophobic chain segments, represented in the above formula by the wavy lines.

A number of ionic or potential ionic compounds suitable for the preparation of PUR-ionomers are available today. The following table gives some typical examples of anionic and cationic internal emulsifiers.

Table 2. Ionic Internal Emulsifiers

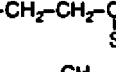
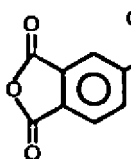
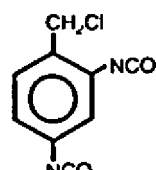
| Sulfonate Types | Lit. Ref. |
|---|-----------------|
| $\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{NH}-(\text{CH}_2)_x-\text{SO}_3\text{Na}$ $x = 2 \text{ or } 3$ | 16-18 |
| $\text{HO}-\text{CH}_2-\text{CH}_2-\text{CH}(\text{SO}_3\text{Na})-\text{CH}_2-\text{OH}$ | 19-21 |
|  (Dimer) | + Base 22-25 |

Table 2. Ionic Internal Emulsifiers (continued)

| Carboxylate Types | | Lit. Ref. |
|---|-------------------------|-----------|
| $\text{HO}-\text{CH}_2-\underset{\text{CO}_2\text{H}}{\overset{\text{CH}_3}{\text{C}}}-\text{CH}_2-\text{OH}$ | + Base | 26 |
| $\text{H}_2\text{N}-(\text{CH}_2)_4-\underset{\text{CO}_2\text{H}}{\text{CH}}-\text{NH}_2$ | + Base | 16, 18 |
| $\text{H}_2\text{N}-\text{CH}_2\text{CH}_2-\text{NH}-\underset{\text{CH}_2-\text{CH}_2-\text{CO}_2\text{Na}}{\text{CH}}$ | | 27 |
|  CO_2H | + Polyol + Base | 28, 29 |
| Cationic Types | | |
| $\text{HO}-\text{CH}_2-\text{CH}_2-\underset{\text{R}}{\text{N}}-\text{CH}_2-\text{CH}_2-\text{OH}$ | + Acid/Alkylating Agent | 16, 18 |
| $\text{HO}-\text{CH}_2-\underset{\text{CH}_2-\text{N}-(\text{CH}_3)_2}{\overset{\text{C}_2\text{H}_5}{\text{N}}}-\text{CH}_2-\text{OH}$ | + Acid/Alkylating Agent | 30 |
|  | + 3° Amine | 31 |

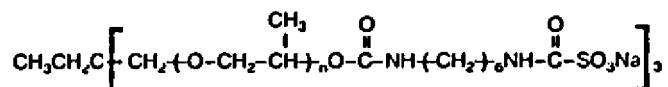
The sulfonate diamines and diols as well as dihydroxy carboxylic acids are the technically most important compounds. Among the dihydroxy carboxylic acids, α,α -dimethylolpropionic acid (DMPA) is found frequently in the literature as a potential ionic building block. The advantage of this compound lies in the steric hindrance of the COOH group which prevents it from reacting with the isocyanate groups. Such reactions would be undesirable because they would consume the potential ionic groups and cause high viscosities due to branching of the polyurethane. Besides building it into the macromolecular chain via the isocyanate/hydroxyl reaction, DMPA can also be introduced into a PUR by using it as a component for the polyester (32-34).

Many recent publications deal with the introduction of ionic groups into preformed polyurethanes which contain special reactive sites. For instance, a segmented polyurethane with olefinic double bonds built into the macromolecular chain is epoxidized and then ring opened with a nucleophile like sodium sulfamate (35).

In a similar way, carboxylic groups are introduced by addition of mercaptocarboxylic acid salts to unsaturated polyurethanes (35-37) or by grafting polyether segments with maleic acid (38).

A special technique of introducing sulfonate groups is by reaction of bisulfite salts with NCO-prepolymers, yielding carbamoyl sulfonates (39).

Bisulfite Blocked HDI Prepolymer



When a pH value under 3 is maintained, aqueous dispersions of these ionomers are stable. Upon increasing the pH, the carbamoyl sulfonate groups are hydrolyzed by splitting off bisulfite (40). Though the mechanism involved in this reaction probably does not lead to free NCO groups (41), these compounds formally act as blocked isocyanates.

Variations of the PUR-ionomers are possible by neutralizing the potential anionic groups with mixtures of counterions. For instance, an improvement of the hydrolytic stability of carboxylate group containing polyurethanes is observed when a mixture of volatile and nonvolatile counterions, e.g. ammonium and alkali metal ions, is used (42).

In other cases, thermolabile counterions which decompose upon curing of the polymer are used. This results in a non-hydrophilic polyurethane film. Examples for this technique are cationic resins in which cyanoacetic acid is used as a neutralizing agent (43, 44).

Besides the anionic and cationic emulsifiers, also amphoteric ones have been used. PUR-dispersions can be made at nearly neutral pH by placing both anionic and cationic centers in the polyurethane matrix (45). In another case, a polyisocyanate terminated prepolymer is chain extended with an excess of an aminofunctional triamine/epichlorohydrin adduct and subsequently reacted with cyclic esters or acrylic acid derivatives and then hydrolyzed to render the polymer amphoteric (46,47). Films from these dispersions can be crosslinked when heated through reactions of the halohydrins or with the amino groups and blocked isocyanates.

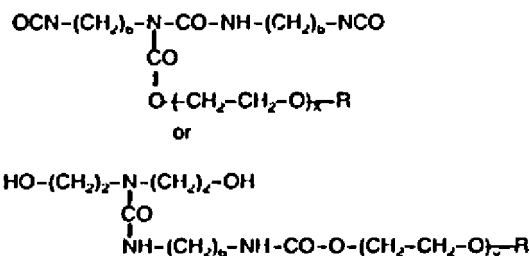
B. 2. Nonionic Internal Emulsifiers

Another way to render a polyurethane water dispersible without external emulsifiers or protective colloids is to attach nonionic hydrophilic polymer segments to the PUR-macromolecule. These are usually water soluble polyether chains made predominantly from ethylene oxide.

Though it appears convenient to replace a part of the hydrophobic macrodiols (which form a large portion of a polyurethane) by polyoxyethylene diols, this technique is not very effective. It is necessary to build so much hydrophilic polyether segments into the PUR-backbones to obtain stable dispersions, that the resulting polyurethane films remain very water sensitive. The dried coatings are often water swellable or even water soluble. In certain cases, products of this type are desirable (48, 49), but for most coatings applications, the water sensitivity should be minimized.

A good compromise between dispersibility of the polyurethanes and water resistance of the dried products is achieved by building polyoxyethylene segments into lateral or terminal positions of the PUR-chain. This can be accomplished by using either modified diols or diisocyanates as building blocks (50-52) or by employing monohydroxyfunctional polyoxyethylene polyethers as such.

Non-ionic Internal Emulsifiers



III. PHYSICAL PROPERTIES OF AQUEOUS POLYURETHANE DISPERSIONS

Aqueous PUR-dispersions are dispersions of polymer particles (typically 10-1,000 nm diameter) in a continuous aqueous phase. Many different internal and external factors have an influence on the stability of a dispersion.

Studies performed by Lorenz (53) prove, that in PUR-ionomer dispersions, the ionic centers are located predominantly on the surface of the dispersed particles, while the hydrophobic chain segments form the interior of the particle. Particle stabilization from this structure can be described by the well known model of the diffuse electrical double layer (54).

At the interface between ionomer particle and water, such a double layer is formed by dissociation of the salt groups. The ionic constituents of the salt group, which are chemically bound to the polyurethane, remain fixed to the particle surface, whereas their counterions migrate into the water phase as far as they are allowed by the attractive forces of the oppositely charged particle surface. This forms a layer of decreasing electrical charge. The interference of the electrical double layers of different particles results in particle repulsion, which in turn is responsible for the overall stabilization of the dispersion.

Evidence for this stabilization mechanism is that PUR-ionomer dispersions coagulate upon addition of inert electrolytes. This behavior can be explained by a compression of the diffuse electrical double layer caused by the presence of additional ions in the water phase. It results in a reduction of the range of double layer repulsion.

An interesting case of an electrolyte effect on the formation of ionic PUR-dispersions has been reported in other studies by Lorenz (55-57). Under certain circumstances, the preparation of PUR ionomers is accompanied by the formation of "polyelectrolytes", i.e., PUR-oligomers containing a high concentration of built-in ionic internal emulsifier. Though it could be expected that these polyelectrolytes support the formation of stable dispersions, they have a negative effect on the particle size and on the stability of the resulting dispersions, paralleling the behavior of simple salts.

If one assumes that PUR-dispersions of the nonionic type have a particle structure similar to that of PUR-ionomers, the hydrophilic polyoxyethylene segments should be positioned on the particle surface "stretching" into the water phase. The stabilization mechanism for this type of particle structure is obviously different from the model of the diffuse electrical double layer.

Alternative theories, such as "entropic repulsion" (58) can be used to explain stabilization of these particles. Entropic repulsion results from the fact that upon close particle approach, the freedom of motion of the polyoxyethylene chains in the water phase is restricted leading to a reduction of entropy.

Additionally, the hydration of the polyoxyethylene chains plays an important role. A particle approaching close enough for coagulation would require the desorption of water molecules resulting in considerable short-range repulsions.

Because of their fundamentally different particle stabilization mechanisms, nonionic and ionic PUR-dispersions show considerable differences in their macroscopic behavior.

Table 3. Factors Affecting Stability of Ionic and Nonionic PUR-Dispersions

| <u>Response to</u> | <u>Dispersion type</u> | |
|---|------------------------|-----------------|
| | <u>Ionic</u> | <u>Nonionic</u> |
| Addition of electrolytes (salts, acids, bases) | Unstable | Stable |
| Freezing | Unstable | Stable |
| Strong shear forces (stirring, pumping) | Partly stable | Stable |
| Temperatures above 70°C | Stable | Unstable |

As seen from this table, nonionic PUR-dispersions have technically important advantages over the ionic ones in terms of stability against electrolytes, freezing, and strong shear forces. On the other hand, they have the disadvantage of being heat sensitive due to the decrease of polyether solubility in water with increasing temperature.

Mixtures of aqueous polyurethanes with ionic emulsifiers and aqueous polyurethanes with nonionic emulsifiers do not offer a solution to this deficiency. It is possible to overcome these problems by combining ionic and nonionic hydrophilic groups in one and the same polyurethane (59-63). The resulting PUR-dispersions possess good heat stability as well as the whole range of other desirable stability features. Especially important is their insensitivity to addition of electrolytes and other additives. These properties allow a wide latitude of formulation to the end user, including addition of pigments, fillers, thickeners, adhesion promoters, flow aids, and crosslinkers.

The combination of ionic and nonionic hydrophilic groups also provides a synergistic effect on the dispersion stability (59). Stable dispersions are obtained using a lesser total amount of emulsifiers. Resulting films have a minimum of overall hydrophilicity approaching properties comparable to those of polyurethanes from organic solution.

PUR-dispersions of this type can be prepared by using mixtures of the aforementioned ionic and nonionic internal emulsifiers as starting materials or by using special building blocks which contain both ionic and polyoxyethylene segments in one and the same molecule (64).

Typically, in both ionic and nonionic PUR-dispersions, the particle size decreases as the amount of hydrophilicity increases. This results in more stable dispersions; however, it also causes an increase in the number of dispersed particles and higher dispersion viscosities.

One of the main advantages of aqueous polymer dispersions is that the viscosity of the dispersion is normally independent of the molecular weight of the polymer. Thus, aqueous PUR-dispersions can be prepared at a high solids content with a molecular weight high enough to form films with excellent performance solely upon "physical" drying. This means that the film formation occurs by simple evaporation of water even at room temperature.

The following table shows that high molecular weight PUR-dispersions are really unique coatings systems, which combine ease of application in different end-use areas with high performance properties.

Table 4. Technological aspects of waterborne polyurethanes:

- Low solvent or solvent free
- Environmentally acceptable
- Relatively low viscosity at relatively high molecular weights
- One component application
- Low temperature "physical" drying
- Typical polyurethane coatings performance

IV. PREPARATION PROCESSES FOR AQUEOUS DISPERSIONS OF HIGH MOLECULAR WEIGHT WATERBORNE POLYURETHANES

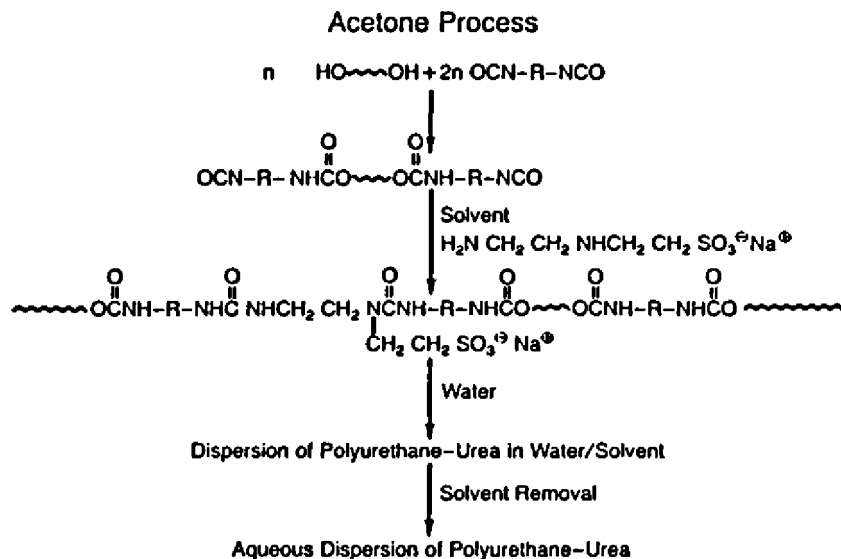
Within the last decade, several new production processes for high molecular weight polyurethane dispersions were developed. Nevertheless, some of the earlier processes also remain technically important. All these processes have in common that their first step is the formation of a medium molecular weight prepolymer with terminal NCO groups (65).

This prepolymer is formed by reaction of suitable di- or polyols with a molar excess of di- or polyisocyanates. It is possible, but not in all cases necessary, to render hydrophilicity to the prepolymer by incorporation of a small portion of internal emulsifiers. Alternately, a suitable amount of internal emulsifiers must be present in the chain extender mixtures if the prepolymer does not already contain sufficient hydrophilic groups.

The critical step in which the various processes differ is the high molecular weight build-up. As this "chain extension" step is normally performed using amines, two main problems have to be dealt with: the control of the extremely fast NCO-NH reaction and the control of the viscosity build-up upon increasing the molecular weight.

A. Acetone Process

This well established process uses an organic solvent (normally acetone) as an intermediate aid to control the viscosity during the critical chain extension step. A high molecular weight polyurethane-polyurea ionomer is built up in an organic solution, as shown below.



The dispersion is formed by addition of water to this solution until water becomes the continuous phase. After removal of the solvent by distillation, a purely aqueous dispersion is obtained. The transformation of the organic polyurethane solution into an aqueous dispersion is a complex process, which occurs by precipitation of the hydrophobic segments or by phase inversion of an intermediately formed inverse emulsion (66). A detailed description of this process is given by Dieterich (2).

Acetone is an especially suitable solvent for this process because it is inert with respect to the polyurethane forming reactions, water miscible, and a low boiling solvent which is easy to remove in the distillation step. An additional advantage of acetone is that it reduces the high reactivity of the amine chain extenders with isocyanates through reversible ketimine formation.

An improvement for the acetone process has recently been proposed using NCO-prepolymers which are made substantially free of monomeric diisocyanates (19, 67) by using thin layer evaporation technology. This avoids the formation of polyelectrolytes, i.e. oligomers formed from monomeric diisocyanates and ionic chain extenders, which have a negative effect on the dispersion stability. In fact, the dispersions obtained from monomer-free NCO-prepolymers showed a smaller average particle size and a lower degree of polydispersity when compared to similar dispersions from untreated prepolymers.

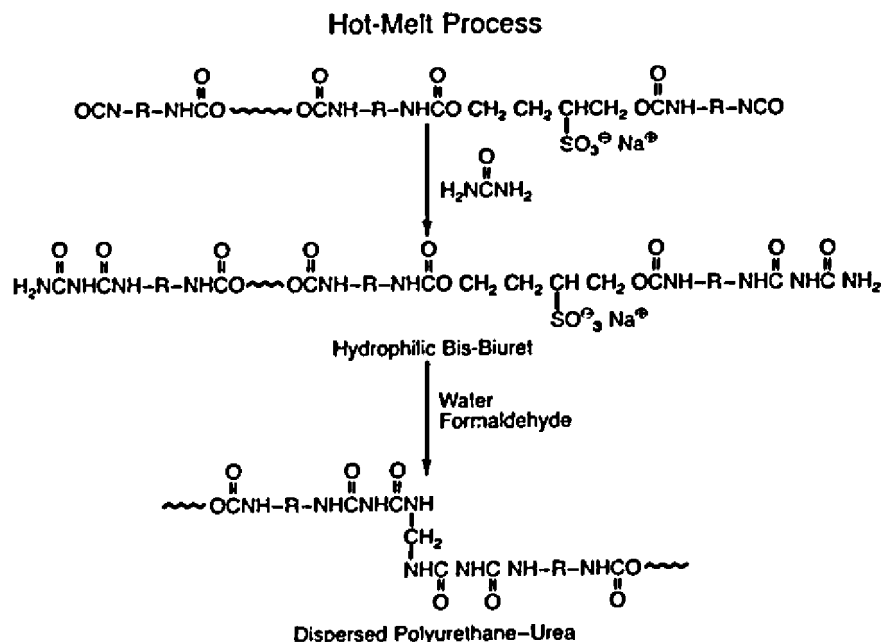
The acetone process allows for very reproducible production of PUR-dispersions because the polymer formation is accomplished in a homogeneous solution.

There are, however, some disadvantages. This process is restricted to predominantly linear polyurethanes (68) which are soluble in acetone prior to the dispersion step. The resulting coatings are usually not very solvent resistant. Besides this, the use and distillation of large amounts of acetone is economically unfavorable. Low reactor volume yields and high energy consumption during distillation are obvious disadvantages.

Alternative processes for the production of PUR-dispersions are designed to be feasible without or with substantially reduced amounts of organic solvents.

B. Melt Dispersion Process (2)

In this process (69), the problems related to the amine chain extension are avoided. The final molecular weight build-up is achieved by an aminoplast polycondensation reaction. As shown in the following figure, an NCO-prepolymer containing ionic groups is reacted with an excess of urea to form biuret end groups. This capped oligomer, which no longer contains any reactive NCO-groups, can be readily dispersed in water without any organic cosolvent.



The reaction with urea is carried out at temperatures above 130°C and the resulting oligomer is usually dispersed at sufficiently high temperatures (approx. 100°C) to warrant a manageable low viscosity. After the dispersion step, chain extension is accomplished by methylation of the biuret groups with formaldehyde and subsequent lowering of the pH or heating to initiate the polycondensation reactions. Alternately, the methylation can also be performed before or during the dispersing step.

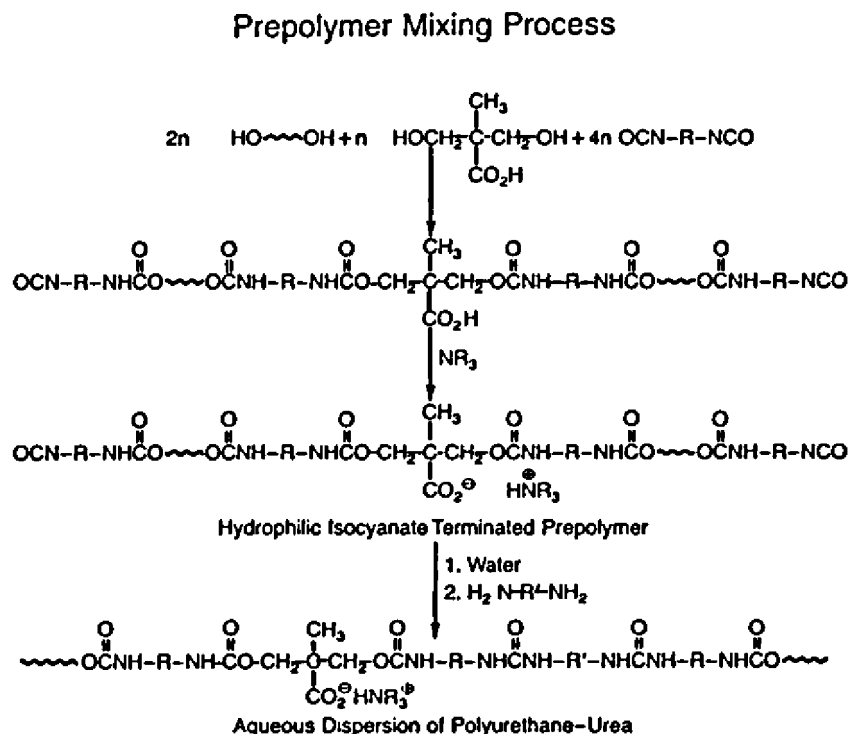
Modifications of the described processes involve the use of prepolymer capping agents other than urea. Ammonia or primary amines yield urea end groups which can be methylolated and crosslinked as well (70). Also, organic dihydrazides have been described as formaldehyde-reactive NCO-capping agents (71).

The melt dispersion process is useful for the manufacturing of aqueous PUR-dispersions with a certain degree of branching in the macromolecular structure. The formaldehyde reaction is difficult to control in a way that acidification or heating will result in a solely linear chain extension. In addition, side reactions involving urethane groups in the PUR-backbone cannot be excluded. Thus, the melt dispersion process yields waterborne PUR with different polymer characteristics than the acetone process.

C. Prepolymer Mixing Process (1,6)

In order to avoid the use of large amounts of solvents and still utilize polyamino compounds in the chain extension step, the NCO-prepolymers must be reacted with polyamines in the presence of water. As pointed out earlier, this is possible due to the difference in reactivity between the NCO-NH and the NCO-H₂O reaction.

Using the so-called prepolymer mixing process, a hydrophilically modified prepolymer with free NCO-groups is mixed with water. Prepolymers made from cycloaliphatic diisocyanates are the most often used due to their low reactivity with water. Chain extension is accomplished by the addition of diamines to the aqueous prepolymer dispersion, as illustrated by the following figure.



For successful utilization of this process, the dispersing step has to be carried out in a short period of time at temperatures below the critical point where the NCO groups start to react rapidly with water. The process also requires careful control of the functionality and viscosity of the NCO-prepolymers (72-74).

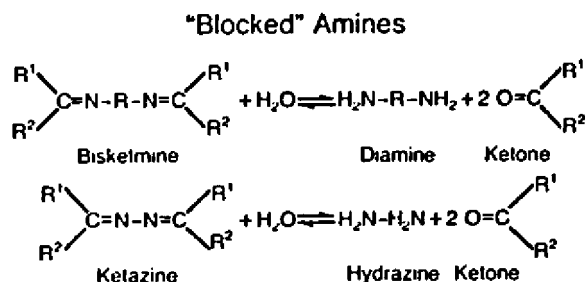
It is often necessary to use some organic cosolvent in this process. Prepolymers containing sulfonate groups are relatively easy to disperse under the required conditions (22).

An advantage of processes which comprise chain extension in the aqueous phase is that the prepolymers can either be reacted with difunctional amines to yield linear, flexible polyurethane-ureas, or with polyfunctional amines (75, 76) to yield crosslinked products. Dispersions of the crosslinked type are especially easy to obtain when the prepolymer contains a combination of ionic and nonionic internal emulsifiers (63). Coatings derived from dispersions of crosslinked polyurethanes show improved solvent resistance.

Waterborne polyurethanes obtained by the prepolymer mixing process are usually somewhat inferior in their elastomeric PUR-properties when compared with products made by the acetone process. This is very likely due to the fact that the chain extension is performed in a heterogeneous phase and therefore does not proceed as smoothly or quantitatively as in an homogeneous organic solution. In order to achieve a quantitative reaction, the amine chain extender has to penetrate by diffusion from the continuous aqueous phase into the interior of the prepolymer particles.

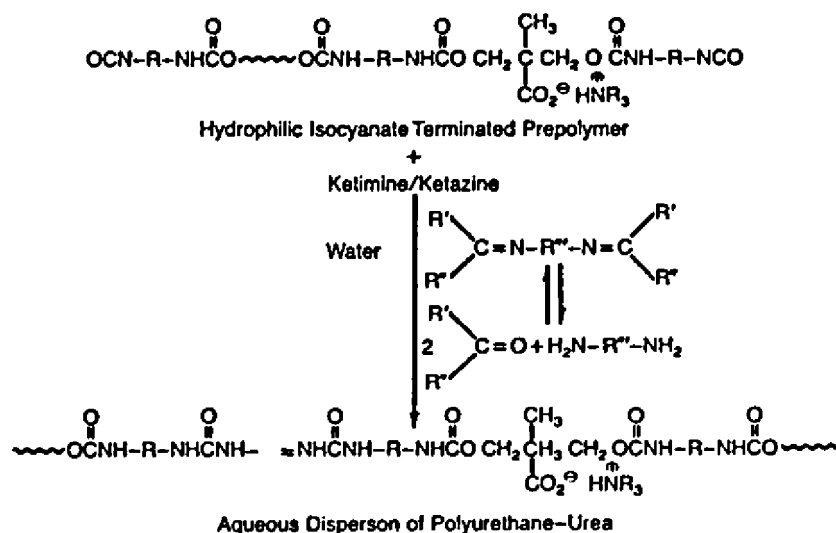
D. Ketimine (and Ketazine) Process (77, 78)

In this process, the amine chain extension occurs homogeneously in the interior of the dispersed NCO-prepolymer particles. This is achieved by mixing the prepolymer with a blocked amine or a blocked hydrazine before it comes into contact with water. Useful as blocked chain extenders are polyketimines or ketazines, i.e. condensation products from polyamines or hydrazine and ketones.



Ketimines or ketazines are in normal processing time and temperature ranges practically inert towards isocyanates. Upon addition of water, free amines or free hydrazines are formed and the systems become reactive.

Ketimine (Ketazine) Process



When mixtures of hydrophilic NCO-prepolymers and polyketimines or ketazines are mixed with water, the chain extension process occurs simultaneously with dispersion formation. In each dispersed particle, the potential reaction partners are already present in the right ratio. The polyaddition reaction, which leads to a high molecular weight polyurethane-urea, occurs smoothly and quantitatively.

Dispersions prepared by these processes yield high performance coatings which approach the quality of waterborne polyurethanes prepared by the acetone process. PUR-dispersions based on aromatic isocyanates, which normally cause problems in solvent-free processes due to their high reactivity with water, are easily accessible.

Besides ketimines and ketazines, also aldimines, aldazines or other compounds forming free amino groups under the influence of water can be used, e.g. oxazolidine derivatives (79).

E. "Other" Processes

There exist many variations of the aforementioned processes. Most of these involve the use of "capped" PUR-prepolymers.

One interesting method to control the critical polyamine chain extension step is to use blocked NCO-prepolymers rather than those containing free isocyanate groups. Oximes are the preferred blocking agents. The process can be performed in the following way. An anionically modified prepolymer with blocked NCO-groups is mixed with a polyamine and dispersed in water. This is followed by heating of the resulting dispersion in order to achieve deblocking of the isocyanate groups resulting in chain extension (80). The main advantage of this method is the same as with the ketazine process—PUR-dispersions based on reactive aromatic isocyanates are accessible without the use of solvents. Crosslinked cationic waterborne PUR can also be prepared by a process of this type (81).

In another example, an excess of polyamine with a functionality greater than two is partially reacted with a blocked NCO-prepolymer prior to the dispersing step. The remaining free amino groups are then neutralized with an acid (82).

Similarly, the preparation of PUR-dispersions can be based on the chain extension of prepolymers capped with an excess of polyfunctional primary or secondary amino compounds. The terminal amino groups can be reacted with epichlorohydrin and acid to yield cationic PUR-dispersions (83-85). They can also be reacted with epichlorohydrin, a dicarboxylic acid anhydride and a base to yield an anionic equivalent (86).

Hydrophilic amino terminated prepolymers can similarly be chain extended by treating them with polyisocyanates (87, 88) after being dispersed in water. Again, the NCO-NH reaction is faster than the NCO-H₂O reaction. An alternate method, in which terminal amino groups are probably also the reactive species, is the chain extension of cationic NCO-prepolymers in the aqueous phase with a polyepoxide (89).

There are still numerous possibilities for producing high molecular weight polyurethanes in an aqueous media. This section and the next one were limited to those which are based on conventional PUR-chemistry and in which the final molecular weight of the polymer film is the same as that in the dispersed PUR-particle. Later sections deal with the post treatment of the polyurethane dispersions, the area of waterborne polyurethane oligomers, and PUR-dispersions which crosslink after evaporation of the water.

V. FILM PROPERTIES FROM WATERBORNE POLYURETHANES

PUR-dispersions can be tailor-made in a way that they yield coatings with the well known properties of conventional solventborne polyurethanes in terms of excellent adhesion, excellent hardness/elasticity relationship, abrasion resistance, gloss, and light stability.

One of the factors which determines the final properties of the polyurethane is the film formation characteristics of the dispersed particles. These particles must fuse or coalesce on the substrate surface at ambient or slightly elevated drying temperatures. Unlike their solventborne counterparts, the dispersion particles must first rejoin into a continuous organic phase before the individual polymer chains can entangle and develop the ultimate film properties. Poor coalescence can result in low gloss films, and usually in a reduction of overall physical properties.

Film forming properties of hydrated swollen polyurethane particles are generally good. They can be somewhat improved by the addition of high boiling coalescent solvents such as N-methylpyrrolidinone or ketones, or by addition of plasticizers. This is often necessary with aqueous dispersions of crosslinked polyurethanes, whose film formation abilities decrease inversely with the crosslink density. Film formation properties also improve with increasing drying temperatures.

The overall film properties are dictated by the selection of starting materials. Best solvent resistance is a result of highest possible crosslink density obtainable, either through hydrogen bonding or covalent linkages. Higher urethane and urea contents typically result in better hardness, abrasion resistance and solvent resistance. Better adhesion and elasticity is gained at somewhat higher content of polyol, although hydrolytic stability may be poor with high polyester contents. Light stability is achieved by using aliphatic isocyanate building blocks, anionic emulsifiers, and avoiding polyether polyols.

Perhaps one disadvantage of aqueous PUR-dispersions is that the emulsifier usually remains in the films. Water swell resistance and hydrolytic stability decrease with increasing amounts of internal emulsifiers.

On the other hand, internal ionic centers also make positive contributions to the polymer properties. Coulombic forces from the ionic centers, similarly to hydrogen bonding, greatly improve the mechanical strength and elastomeric character of the materials (6).

There are two main areas where aqueous PUR-dispersions are generally inferior to solventborne two-component polyurethanes: solvent resistance and water resistance. These obstacles are both difficult to overcome because of the very nature of the dispersions themselves.

Better solvent resistance could be obtained by higher crosslink densities, but two factors limit improvements in this area. Highly branched prepolymers have viscosities too high for them to be mixed with water at normal processing temperatures. Highly crosslinked polymers have high glass transition temperatures and, therefore, will not coalesce to form continuous films at normal drying temperatures.

Better water resistance could be obtained by eliminating the internal emulsifier. Unfortunately, the hydrophobic polymers would no longer form stable aqueous dispersions of particles.

However, it is possible to minimize these disadvantages by using formulations which have a careful balance in terms of the amount and nature of hydrophilic groups and the degree of crosslinking. Table 5 lists the film properties of two different "state-of-the-art" aqueous PUR-dispersions. One is a linear, highly elastic polyurethane adhesive. The other one is a crosslinked, hard surface coating. For comparison, the properties of a flexible two component, solventborne coating are included.

Table 5. Properties of Films Formed from Aqueous Polyurethane Dispersions. (90)

| Film Property | Film Formed From ^a | | |
|-------------------------------------|---|---|---|
| | Impranil DLN ^b Dispersion | Baybond XW-110 ^c Dispersion | Two Component Flexible ^d Coating |
| Pendulum Hardness (sec.) | 30 | 115 | 180 |
| Reverse Impact (in-lbs) | 160 | 160 | 160 |
| 100% Modulus (psi) | 200 | 5200 | 3000 |
| Tensile Strength (psi) | 3000 | 6600 | 4700 |
| Elongation at Break (%) | 700 | 170 | 110 |
| Set (%) | 10 | - | - |
| <u>Volume Swell (%)^e</u> | | | |
| Water | 15 | 0 | 0 |
| 2-Propanol | 52 | 95 | 33 |
| 2-Butanone | 640 | 146 | 95 |
| 2-Ethoxyethyl acetate | 392 | 95 | 73 |
| Xylene | 310 | 73 | 73 |
| 1,1,1-Trichloroethane | 700 | 120 | 95 |

^aFilm properties determined after two weeks drying at room temperature.

^bBayer A.G. (Leverkusen, Germany)

^cMiles Inc.

^dBased on Desmodur N polyisocyanate and Desmophen 670 polyol (Miles Inc.).

^eDetermined after 24 hour immersion in the solvent.

Much work in the area of waterborne polyurethanes has been directed to improve the solvent and water resistance properties of films. The approaches include: post-treatments of the dispersions by the manufacturer or applicator, formation of ambient temperature self-crosslinking dispersions, or incorporation of functionalities which allow further crosslinking upon bake.

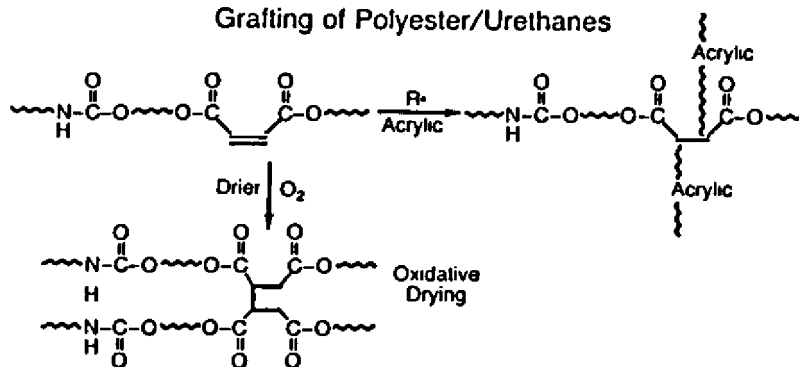
VI. POST TREATMENT OF AQUEOUS POLYURETHANE DISPERSIONS

The objective is to improve the water resistance and mechanical properties of films formed from aqueous PUR-dispersions. The approach is to replace a portion of the typical polyurethane with other types of polymers.

A. Grafting

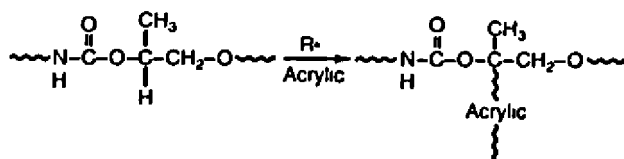
One method is to graft hydrophobic unsaturated monomers onto the polyurethane backbone. Grafting is usually accomplished in the aqueous phase using emulsion polymerization techniques. Monomer and free radical initiation are added to the preformed polyurethane-ureas, which contain unsaturated polyester polyols. Often a higher amount of free radical initiator is used than in normal emulsion polymerizations. Both anionic and cationic unsaturated polyester-urethanes have been prepared (91).

Grafting of Polyester/Urethanes



Cationic polyurethanes, which contain polypropylene glycol in their backbone, have been used to graft acrylate monomers onto the main chain (92). This can also be done prior to the chain extension step in the presence of free isocyanate groups (93).

Grafting of Polyether/Urethanes



Anionic polymers containing polypropylene glycol have also been modified in this manner using acrylate monomers (94, 95), or fluoroalkenes (96) or styrene (97). Anionic polyurethanes, which use carboxylate salts as internal emulsifiers, can be further crosslinked with epoxy resins (98).

Anionic and cationic PUR-prepolymers have been capped with unsaturated alcohols and then chain extended through use of free radical initiators or copolymerized with additional unsaturated monomers (99).

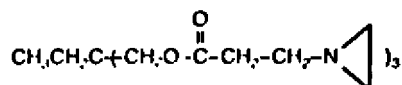
B. External Crosslinking Methods

Grafting of polymers onto polyurethanes is usually done by the resin manufacturers, external crosslinking is done by the formulator prior to the application of the waterborne PUR. In any event, the solvent resistance and water resistance of the resulting film is improved.

Aqueous PUR can be crosslinked in much the same manner as other waterborne polymers. Most reactions center on the carboxylic acids contained in anionic polyurethanes. Polyfunctional aziridines, methoxymethylolated melamine or urea resins, carbodiimides, and polyisocyanates or blocked isocyanates are used.

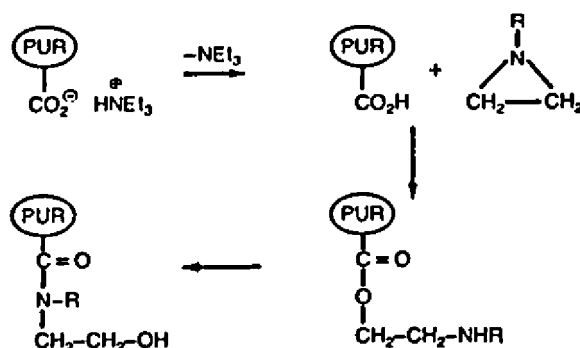
Trifunctional aziridines (example below) have been used quite extensively (100-104). The aziridine must be added just prior to the application of the PUR-dispersion. The aziridine can lose activity after two days storage in water at room temperature. Crosslinking also takes place at room temperature.

Polyfunctional Aziridines



Usually, the intermediate β -amino esters, which are derived from the reaction of polymer bound carboxylic acids with the aziridine, rearrange to form the more stable β -hydroxyamides (105).

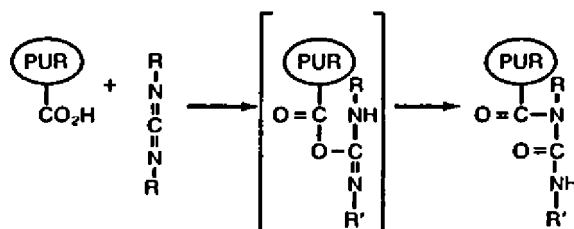
Crosslinking With Aziridines



Crosslinking also takes place at room temperature upon post addition of polyisocyanates (106,107). Here aliphatic isocyanates are preferred to reduce formation of polymeric ureas from the water reaction. The formation of amides (from carboxylic acids), allophanates (from urethanes), and biurets (from ureas) all contribute to higher molecular weight buildup and crosslinking.

Room temperature crosslinking can also be accomplished by using waterborne polycarbodiimide crosslinkers. The chemistry takes advantage of the carboxylic acids attached to the polyurethane backbone. Externally emulsified polycarbodiimides (108) and ionically modified polycarbodiimides (109) have both been described.

Crosslinking With Carbodiimides



Polyurethanes can also be crosslinked upon baking. Methoxymethylated melamine/formaldehyde (MMMF) and urea/formaldehyde resins (110) are claimed useful for cationic polyurethanes. Anionic urethanes have been crosslinked by baking with water dispersible blocked polyisocyanates (111) or with mixtures of blocked isocyanates and MMMF (112) or urea/formaldehyde resins (113).

VII. SELF-CROSSLINKING WATERBORNE POLYURETHANES

An internal means of crosslinking is obtained by incorporating reactive species in the interior of the polymer backbone, or on the interior of the dispersed polymer particle. It is also possible to use the hydrophilic polyurethane prepolymer as an emulsifier or protective colloid for other reactive oligomers.

A. Oxidative Drying

Perhaps the most obvious way to make self-crosslinking waterborne polyurethanes is to produce waterborne uralkyd resins. These materials, like solventborne oil-modified urethanes (or urethane modified alkyd resins), cure by free radical reactions of unsaturated hydrocarbons with atmospheric oxygen in the presence of metallic driers or siccatives. The unsaturated hydrocarbons are usually introduced as part of the polyol portion during prepolymer formation, but can also be introduced by capping the isocyanate functional prepolymers.

One simple method uses external emulsifiers to disperse a hydrophobic uralkyd. Graft copolymers of ethylene oxide and acrylic acid/acrylate ester (114, 115), as well as simple acrylics (116), have been used as anionic emulsifiers for urethane oils.

A more generally used method is to build the emulsifier internally in the uralkyd itself. One unusual example describes a carboxyl functional acrylic to neutralize a tertiary amino functional uralkyd resin (114, 117). More common is to produce anionically modified polyurethanes replacing a portion of saturated polyol with polyols based on maleic acid (118), esters prepared from ethers and maleic acid (38), acrylic graft copolymers based on maleic acid (119), linseed oil based polyesters (120), or even alkyne containing polyols (121). Dispersions of this type may also contain saponified shellac as a second resin component (122).

It is also possible to use the alkyd resin as a building block for the ionic emulsifier source. Half esters of partially hydrolyzed triglycerides and trimellitic anhydride have been used (123). Alkyd resins (124) as well as oil modified polyester-amides (125) have also been "acidified" with polycarboxylic acid anhydrides. The resulting PUR-dispersions are generally of lower molecular weight.

Lower molecular weight materials are also obtained when the polyurethane prepolymer is capped with an unsaturated alcohol rather than being chain extended with a polyfunctional amino compound. Nonionic externally emulsified polyurethanes capped with allyl alcohol (126), cationic (127), and anionic (128) internally emulsified polyurethanes capped with hydroxyethyl (meth)acrylates, and anionic acrylic externally emulsified diisocyanate/hydroxyethyl (meth)acrylate adducts have all been investigated.

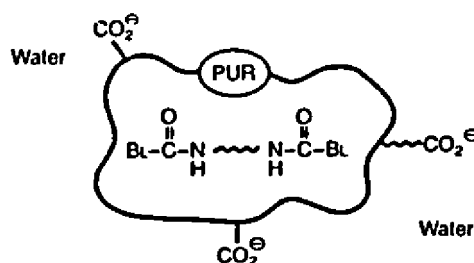
The properties of waterborne uralkyds are similar to those of their solventborne counterparts. Compared to conventional alkyds, the incorporation of urethane linkages speeds up the drying of the films and improves the gloss and abrasion resistance of coatings based on them. They are still basically alkyd resins and the properties do not meet the standards of two component solventborne PUR-coatings. It is possible to upgrade the properties by incorporating higher amounts of urethane linkages.

Higher quality uralkyds can be prepared using a combination of oxidative cure and curing with blocked isocyanates upon baking (113).

B. Codispersed Hydrophobic Crosslinkers

The principle here is to use the aqueous PUR as a protective colloid or as an external emulsifier for another compound. These compounds are usually polyfunctional and react with portions of the (co)dispersed polyurethane matrix, normally upon baking. They are mixed with the emulsifier and then codispersed in water. The amount of these hydrophobic crosslinkers which can be codispersed with the hydrophilically modified PUR is limited. If too much is added, precipitation or gelling of the material can occur.

Codispersed Hydrophobic Crosslinkers



Films with good resistance to water and humidity can be made by codispersing carnauba wax with a hydrophilic urethane (129). In this case, the codispersed wax does not react with the polyurethane, but rather makes the total polymer composition more hydrophobic.

Crosslinked polyurethanes are obtained upon baking films based on aqueous PUR-dispersions containing codispersed hydrophobic blocked polyisocyanates (130, 131). Other hydrophobic crosslinkers (such as aminoplast resins) can be substituted for a portion of the blocked polyisocyanates. It is also reported that crosslinkers containing both blocked isocyanates and unsaturated hydrocarbons in the same molecule are effective (132).

Cyanamide crosslinkers have also been codispersed into ionic urethanes. Tollycyanamide is claimed effective in cationic PUR-dispersions (133), while polycarbodiimides are especially effective for carboxylate containing anionic polyester-urethanes (134).

Epichlorohydrin derivatives are another class of crosslinkers for ionic polyurethanes. The triglycidyl ethers of polyhydric alcohols (e.g. glycerine) have been codispersed in cationic polyurethanes to provide crosslinked films upon baking (135).

Common to all of these approaches is that the unmodified crosslinkers cannot simply be added to the finished aqueous PUR-dispersion. The manufacturer must add them prior to the dispersing step. Thus, the applicator has limited control of the crosslink density of the system. Additionally, many of the systems are sensitive to high shear forces and to formulation additives.

C. Other Internal Crosslinking Methods

Most of the "other" internal crosslinking methods involve chemistry which was described earlier in this chapter. The main feature here is that the final molecular weight buildup takes place on the substrate rather than in the manufacturer's vessel. This avoids high prepolymer viscosities and problems associated with film formation of crosslinked dispersed particles. In most cases, the films must be baked.

Perhaps the simplest method for accomplishing this type of crosslinking is to use high amounts of carboxylic acids in forming an anionic prepolymer and then capping the isocyanates with an excess of polyfunctional amines. Crosslinking takes place through the formation of amide linkages upon baking (136).

Another method is to use anionic polyurethanes which have been capped with polyamines and then reacted with less than molar amounts of partially blocked polyisocyanate adducts. At elevated temperatures, the excess amine displaces the blocking group. Aliphatic (137), cycloaliphatic (138), and aromatic polyamines (139) have been used.

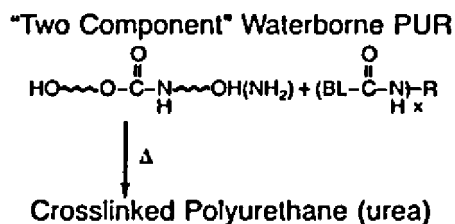
The previously described method is probably more effective using cationic polyurethane prepolymers in cationic electrodeposition formulations. Here the acidic counterion for the potential cationic center (usually tertiary amine) also neutralizes the amino capped prepolymer. Again the capped prepolymer is reacted with less than the required amount of partially blocked polyisocyanate (140) or alternatively with halohydrins (135) as previously mentioned (85).

The same method has also been described for nonionic PUR-dispersions (141).

Mannich bases (142) or amino functional heterocyclic compounds (143) have been used as the amine capping agent, especially for cationic PUR-dispersions.

Besides amino capped polyurethane prepolymers, hydroxyfunctional ones have been described. Beta-hydroxy urethanes are reported to cure upon heating without any additional "blocked" polyisocyanate (144). Here the β -hydroxy urethane itself probably acts as a blocked isocyanate.

More commonly, the hydrophilic hydroxyfunctional polyurethane is admixed with a hydrophilic blocked isocyanate functional polyurethane (145). These combinations have excellent pigmentability and baked films have properties much like their solventborne counterparts.



Acrylic equivalents have been described (146) where the hydroxy- and blocked isocyanate-functionalities are combined in the same polymer molecule. Acrylate monomer mixtures containing both hydroxyethyl acrylate and blocked isocyanato methacrylate are copolymerized to form thermosetting ionic acrylic dispersions.

Another approach utilizes special "blocked" isocyanate raw materials. The uretedinediones (or dimers of isocyanates) can be considered as isocyanate splitters. The dimers are stable within the particles dispersed in aqueous solution, but react with hydroxyl compounds when heated. The dimers of toluene diisocyanate (147) and isophorone diisocyanate (148) have both been incorporated into hydroxyfunctional prepolymers with the uretedinediones providing the crosslinking sites.

There are two methods which utilize sulfur containing compounds as a means of crosslinking. The first involves an ene-thiol reaction in which pendant mercapto groups react with maleic acid derivatives contained in the PUR-backbone (149). The second approach utilizes hydrazinoalkyl hydrogen sulfates as a crosslinking agent (150). These methods are somewhat unique in their chemistry.

The difference between this section and the next one is that the self-crosslinking dispersions already contain both reactive species before the dispersion is applied by the end user. Waterborne oligomers are supplied with only one reactive functionality. The choice of coreactants is left to the formulator.

VIII. WATERBORNE POLYURETHANE OLIGOMERS

The most common waterborne PUR-oligomers are the amino, hydroxyl or blocked isocyanate functional hydrophilic urethanes.

Amino-functional hydrophilic urethanes can be crosslinked with blocked isocyanates or with waterborne epoxy resins (151,152). They can also be used to crosslink epoxy functional polyurethanes (153).

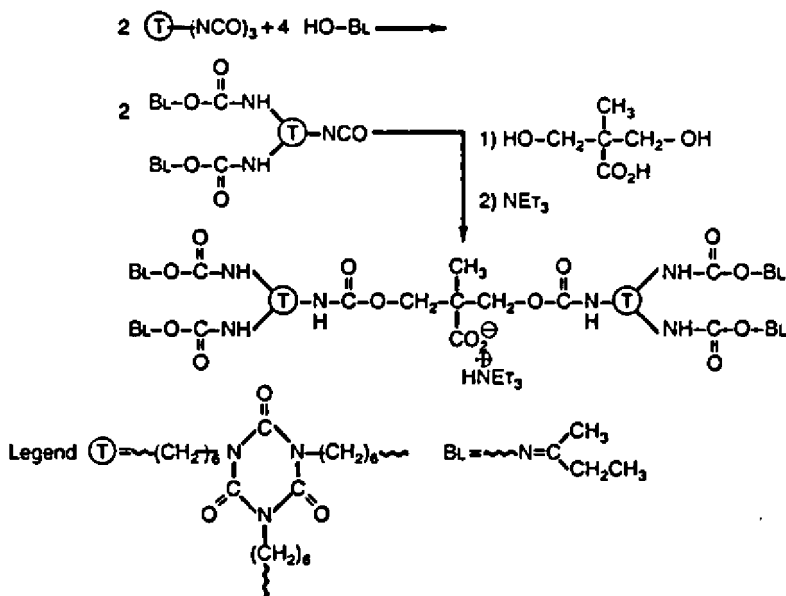
Nonionic externally emulsified hydrophobic acrylic polyols (154) and nonionic internally emulsified polyesters (155), polyether-esters (156), or polyethers, polyesters, or polycarbonates partially reacted with cyclic anhydrides (157) can be crosslinked with blocked polyisocyanates. Anionic polyester-urethanes have also been crosslinked with water soluble aminoplast resins (158).

A special class of waterborne polymers are hydrophilically modified solid polyurethanes. These oligomers generally have enough hydrophilic character so that they will spontaneously disperse in water. Hydroxyfunctional (159), mercapto and olefinic (160) containing polymers have been reported. Also, isocyanate functional anionic uretedinediones (161), nonionic isocyanate functional (162) and anionic blocked isocyanate functional (163, 164) solids are reported.

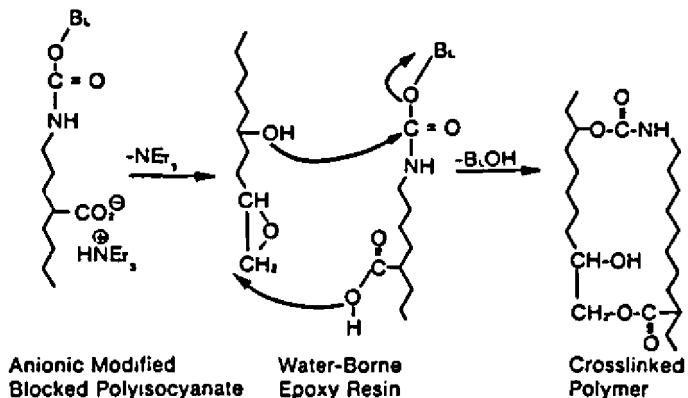
Aqueous emulsions of hydrophobic blocked polyisocyanates can be prepared by using an external emulsifier prepared from monofunctional ethoxylated fatty alcohols, polyisocyanates and sodium bisulfite (165).

Other anionic hydrophilic blocked isocyanates are made with internal emulsifiers. Hydroxyfunctional carboxylates have been capped with partially blocked polyisocyanate (111) as shown below. Amino-sulfonate emulsifiers can also be used (166). Virtually any blocking group has been described (41). These materials are useful for crosslinking hydroxyfunctional acrylic polymers or acrylic/vinyl copolymers (167), epoxy resins as shown below (168, 169), as shown below, and almost any hydroxyl-containing compound (170). It is even possible to ship these type materials prior to dispersing them in water, making transportation less costly (171).

Blocked Polyisocyanates

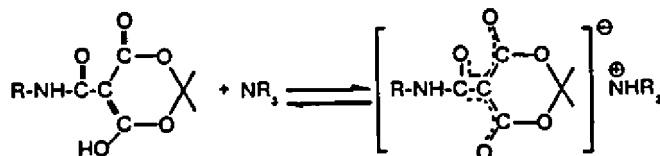


Dual Curing Urethane/Epoxy

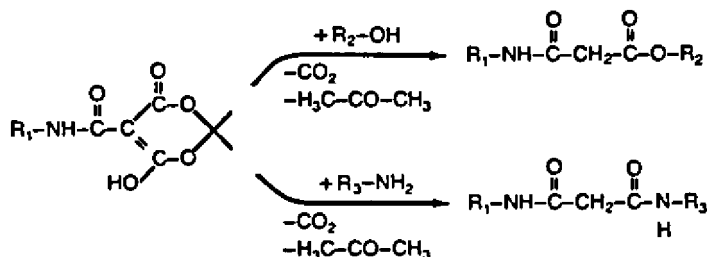


There is one special case in which, similarly to sodium bisulfite, the blocking agent acts as the emulsifier source. The remaining proton on the Meldrum's acid (isopropylidene malonate) blocked polyisocyanate adducts is so acidic that it can be neutralized with amino compounds. Volatile amines split off as the crosslinker functions upon bake (172).

Meldrum's Acid Blocked Isocyanates



Reactions of Meldrum's Acid Blocked Isocyanates



This concludes the discussion of the chemistry of waterborne polyurethanes. As mentioned before, much of this chemistry was developed to make specific products especially suited for use in specific application areas. The last section shows the driving force for these developments. The impetus for these developments comes from the application areas which are described in the following section.

IX. APPLICATION AREAS

The earliest use for aqueous PUR-dispersions, i.e. as a coating for textiles, is still one of the largest market areas for them. Typically, the nap side of woven or knitted fabric is coated using a direct or transfer coating process (112, 131, 173).

In the transfer coating process, a topcoat is applied by doctor blade onto grained or smooth siliconized paper, dried, coated with an adhesive layer, and laminated onto the textile. Finally, the coated material is removed from the release paper.

Some interesting variations of this process are possible during the application of the PUR-dispersions. Foamed adhesive coats, which can be obtained by mechanical frothing of nonionic PUR-dispersions (174), yield articles with a very soft feel and elegant drape without requiring expensive roughened fabrics.

Alternately, foamed interlayers can be obtained from PVC-pastes which contain blowing agents. These are applied onto waterborne PUR topcoats and foamed "in situ". PUR-dispersions can be designed to provide a barrier against migration of the plasticizers from the PVC while withstanding the high temperatures required for the "gelation" of the PVC (175, 176).

A new version of the transfer coating process uses thermoactive, crosslinkable PUR-dispersions. These materials can either be applied as adhesive coats (177) or as heat reactivable topcoats (116). The latter results in a one-coat transfer coating process.

Lightweight fabrics with a comfortable hand (feel), high flexibility and elasticity, good abrasion resistance, and a unique combination of water barrier yet air- and water-vapor permeability can be used as rainwear, clothing, footwear, tent materials, and carrying cases (4).

Coagulation of films of aqueous PUR and subsequent lamination onto textiles results in porometric (porous) materials used as leather substitutes. Sometimes a foam layer is placed between the textile and the laminate to provide a more comfortable material for shoe uppers (178).

The coagulation can be achieved through several processes. The heat coagulation of nonionically modified hydrophilic PUR- (179) or ionically/nonionically modified PUR-dispersions containing electrolytes (62), the elimination of the ionic center in anionically (180-183) or cationically (184) emulsified PUR, the precipitation of the hydrophilic PUR by addition of nonaqueous materials (185, 186), or the crosslinking of mainly linear polyurethanes. Epoxy (187), aminoplast resins (188), and blocked polyisocyanates (189, 190) are used as crosslinking agents.

The quality of split leather can also be increased by using aqueous PUR-sizing treatments in a tanning process (191, 192).

Textile fibers can be impregnated (sized) with aqueous PUR to improve their properties. This treatment can provide fabrics with increased tensile strength and resistance to dry cleaning solvents (193, 194) and aqueous detergent solutions (195). Dyeing properties of some fabrics can also be improved (196). The impregnation renders polyester and cotton fabrics wrinkle resistant (197, 198).

The treatment of wool fibers with aqueous PUR results in material with decreased pilling and shrinkage (199). Typically aqueous solutions of alkali bisulfite blocked polyisocyanate prepolymers such as Synthapret[®] BAP dispersion are used for this application (200).

Paper fibers are sized with aqueous PUR to increase the strength of the paper as well as to reduce the tendency of ink to run on the surface (201-203). High strength cardboard with resistance to fats and oils (122, 204) is produced by coating cardboard with emulsified blocked PUR-prepolymers or with unsaturated ester-containing PUR (205). Carbonless carbon paper can be produced by coating dispersed microencapsulated ink capsules onto paper using aqueous PUR-vehicles (206).

Polyurethane latices are useful carriers for photographic developers (207) used on photographic papers. They have also been found suitable as plasticizing additives for photo gelatins (208-210) or for photographic layers (129, 211).

Polyurethanes, especially isocyanate- or blocked isocyanate-containing materials, show excellent adhesion to cellulosic materials (wood fibers). Nonionically emulsified diphenylmethane diisocyanate based products are used as binders for wood chips to make particle board (107, 212-214). Sodium bisulfite blocked polyurethanes have also been claimed effective in this area (215). Wood coatings, especially for flooring, are made using aqueous PUR (216) as such or in combination with waterborne acrylics. They provide coatings with high gloss, abrasion resistance and are unaffected by most household cleansers.

Textile, leather and cellulosic fibers can all be sized with solventborne polymers. The manufacturing process for the production of glass fibers however, precludes the use of solvents. Only waterborne materials can be used to prevent explosive vapor build-up at the high processing temperatures.

Typically, nonionically (excellent electrolyte stability) or cationically modified polyurethanes are used (217-222). The polar groups in the aqueous PUR provide excellent adhesion to glass surfaces as well as to the surfaces of most polymers, e.g. polycarbonate and polyamide, in which the glass fibers are incorporated to manufacture composites with high modulus and tensile strength. The PUR are sometimes combined with epoxy resins (223) and often used with silane coupling agents (224-226).

Aqueous PUR have also been suggested to provide shatterproof coatings for glass bottles (227, 228), glass lamps (229), and cathode ray (TV) tubes (230). Glass has previously been a difficult surface to coat because it is extremely smooth and solvents do not "bite" into it to provide good adhesion (231).

Conversely, solvents aggressively attack many plastic surfaces. Thus aqueous PUR-dispersions with good adhesion properties (232, 233) are valuable materials for plastic coatings. Waterborne PUR are used to increase the abrasion resistance, decrease blocking (234-236) of polyvinyl chloride (e.g. for upholstery fabric) and other vinyl resins used in the flooring industry (100). Aqueous PUR are also useful coatings for disposable foamed polystyrene cups (237). They have been proposed to coat reaction injection molded PUR-parts used in the automobile sector (238, 239).

Another area where aqueous PUR could be used to coat plastics is in the magnetic tape industry. PUR-emulsions containing dispersed magnetic particles can be coated onto polyethylene terephthalate films (240-244). The thermoplastic urethanes allow a high loading of and mobility of the magnetic particles in the finished polymer, but have sufficient hardness and abrasion resistance to prevent fouling of the magnetic recording apparatus.

Aqueous PUR have long been used as adhesives (245), especially for polymeric substrates (246). Typically, dispersions of linear PUR are mixed with other polymers to lower cost. Polyvinyl acetate (247), phenolic resins (248), epoxies (249, 250), and acrylics have all been admixed with aqueous PUR. Often, aminosilane coupling agents (251) are added to improve adhesion properties.

Ionically modified PUR even have good adhesion to natural and synthetic rubber surfaces (252) and can be used in the manufacture of footwear (253). Dispersions of thermoplastic PUR are successfully used to bond PUR-foam to metal (254). Two-component, thermosetting PUR using blocked isocyanates have also been used as adhesives (151, 255, 256).

Water swellable materials prepared from aqueous PUR have found use as caulking materials for sewer sealants (257) and on synthetic rubber substrates (258).

Hydrophilic PUR have been used as media in which monomers have been polymerized (259-261). Cationic PUR have been used for the emulsion polymerization of styrene (262); anionic ones for butyl acrylates (263); nonionic ones for polyenes (e.g. trimethylolpropane triacrylate) (264).

Some waterborne paint additives are also made from aqueous PUR. Defoamers (265) and associative thickeners (266-269) have been prepared from nonionically modified PUR; pigment pastes (270) and textile dyes (271, 272) have been made most often from anionic ones.

Last but not least, waterborne PUR are penetrating the important area of metal coatings. Examples are their use as metal primers (113, 130, 145, 273), as coil coating resins (274), and as wire coatings (275, 276).

The important area of cationic electrodeposition coating should also be mentioned (277-280). This technology is widely used for automotive metal primers providing excellent corrosion resistance to car bodies. Cationic electrodeposition resins can formally be regarded as waterborne polyurethanes though they usually contain only a small concentration of urethane linkages.

Epoxy resins are modified with amines, and then either quaternized or neutralized with acids to provide cationic centers. The curing of these coatings is accomplished by use of blocked isocyanates either reacted into the epoxy resin backbones or codispersed with the cationically modified epoxy.

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Exhibit A